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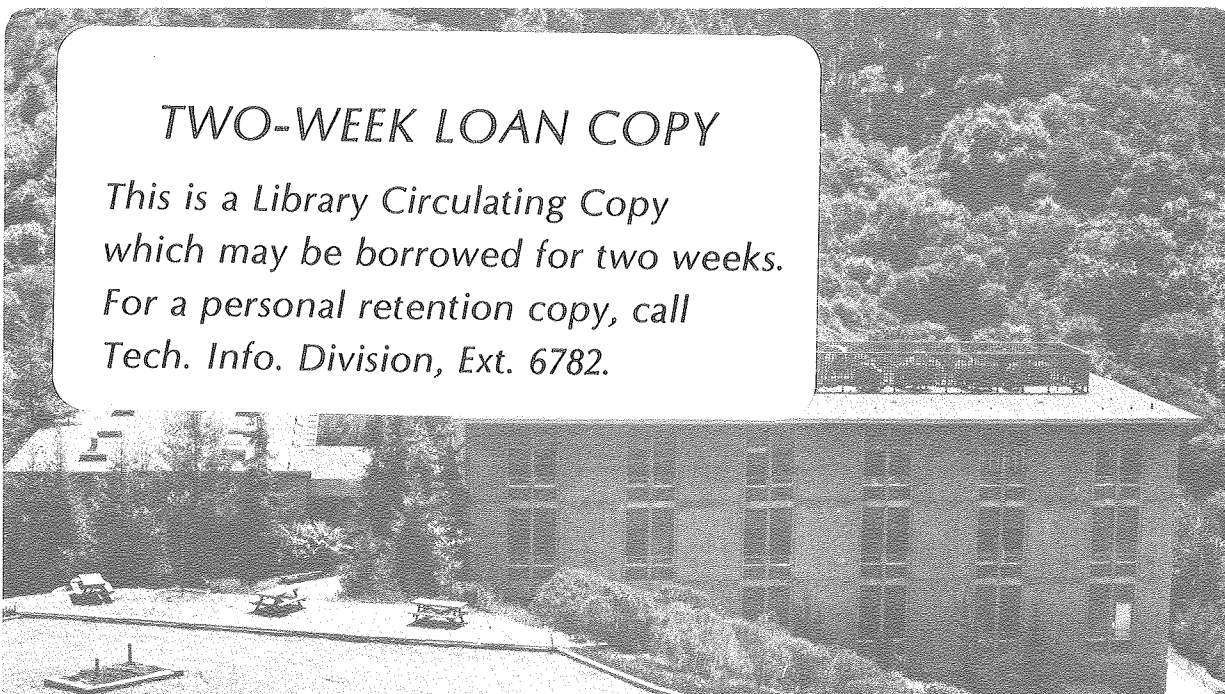## Materials & Molecular Research Division

LASER-INDUCED DISSOCIATION OF MONOMERS AND DIMERS OF BROMINE

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Abstract

In recent years various aspects of laser-induced processes in
molecules have been studied. In our laboratory we used
photofragment spectroscopy in order to probe excited states of
bromine. The crossed laser and molecular beams experiment is
described. The results on the monomer dissociation are discussed
and compared with previous studies. In addition, the dissociation
of dimers has been investigated for the first time using the same
technique, and preliminary results are presented.

Photofragment spectroscopy has been shown to be a suitable method for dissociation studies of molecules [1]. In this paper we would like to report experiments that have been performed on bromine in our laboratory. A crossed laser and molecular beams arrangement has been used for the excitation of the bromine molecules. Our setup is similar to the one described in [2]. Briefly, the supersonic molecular beam is formed by expansion of a Br_2/Ar gas mixture at a total stagnation pressure of 260 Torr from a 0.1 mm diameter quartz nozzle. The Br_2 molecule density in the beam is controlled by a constant temperature bath surrounding the bromine reservoir. The nozzle can be heated and its temperature monitored during the experiment. By introducing different skimmers along the beam, its diameter at the inter-section with the laser beam is kept at approximately 2 mm.

We used two linearly polarized lasers for our experiments, both with a linewidth of 1 cm^{-1}. First a frequency-doubled, pulsed Nd:YAG laser (Quanta Ray) with a wavelength of 5324 Å, a pulse width of 10 ns and a pulse energy of up to 200 mJ. Thus at a pulse repetition frequency of 10 Hz the maximum average power was 2 W. In addition a flashlamp-pumped, selfmade tunable dye laser was used. Its output consisted of pulses with 600 ns width and a maximum energy of 20 mJ yielding 200 mW average power at 10 Hz. This laser was operated with Coumarin 480, solved in a methanol/water mixture of 1 : 1.

With the aid of an interference filter it was tuned to a wavelength of 4844 Å. The absorption into the continuum of the B 0_u^+ ($^3\Pi$) electronic state of Br_2 peaks at this wavelength.

The photodissociation fragments were analyzed by a detector which was located several centimeters away from the intersection volume. The detector consists of an ionizer, a quadrupole mass spectrometer, and a gated counting system. In contrast to the setup described in [1], our detector can be rotated within the plane given by the laser beam and the molecular beam around an axis perpendicular to this plane through the intersection point. Therefore, angular distributions of fragments can be recorded with a resolution better than $\pm$ 0.5°. Velocity distributions of the fragments were measured with a 256-channel scaler which was gated by the laser pulse. Usually, a time-of-flight spectrum was taken for a given mass and angle.

At a wavelength of 5324 Å (18783 cm^{-1}) only ground state bromine atoms can be produced either by absorption into the continuum of the A 1_u ($^3\Pi$) state and subsequent dissociation or by absorption into a discrete level of the B 0_u^+ ($^3\Pi$) state followed by predissociation. By changing the polarization of the laser beam from vertical to horizontal the two processes can be distinguished because the A $\leftarrow$ X transition is perpendicular whereas B $\leftarrow$ X is a parallel transition. In this notation X means the electronic . . .

. . . ground state which is a O_g^+ ($^1\Sigma$) state. At vertical polarization the time-of-flight spectrum for Br shows a narrow peak. The corresponding flight time is in agreement with the velocity of the bromine atoms calculated from the excess energy $\Delta E = h\nu - E_{diss}$, where $h\nu$ and E_{diss} represent the photon energy and the dissociation energy respectively. Since the fragments are atoms, all the excess energy is transformed into translational energy. Thus the width of the peak in the time-of-flight spectrum reflects the velocity distribution in the original molecular beam. In fact, the position of this peak can be used to calibrate the velocity of the molecular beam which has also been measured independently. This velocity is $5.2 \cdot 10^4$ cm s^{-1}. The measured dependence of the time-of-flight spectrum on the polarization of the laser beam indicates that predissociation does not contribute to the fragmentation at this particular wavelength. This is in agreement with the observations made by Oldman et al [1] and is not surprising mainly for two reasons. First, we may not hit a discrete level in the B state which favours predissociation. It is known [3], at least for iodine, that the predissociation rate strongly depends on the vibrational, the rotational and even on the hyperfine level excited. Second, F. Zaraga et al [4] conclude from their studies that the optimum wavelength range for predissociation of bromine is near 5580 Å. Nevertheless we observed several peaks in the time-of-flight spectrum at horizontal laser polarization which have to originate from a B ← X transition.

One of the peaks is due to the absorption of two 5324 Å photons yielding one ground state Br ($^2P_{3/2}$) and one spin-orbit excited Br* ($^2P_{1/2}$) atom. Whereas this two photon process has also been reported in [1], the additional peaks that we observed have not been mentioned. They correspond to slower velocities indicating smaller excess energies. Our analysis of the corresponding flight times shows that they arise from hot band absorption. Starting from $v'' = 3$, 4 etc. in the electronic ground state, the photon energy is large enough to exceed the dissociation threshold of the B state and thus absorption into the continuum of the B state occurs. This process results in the production of "slow" Br ($^2P_{3/2}$) and Br* ($^2P_{1/2}$) atoms. Although only 2.4% of all the molecules are in the $v'' = 3$ state at the nozzle temperature of 407 K, the corresponding signal in the time-of-flight spectrum is very distinct. The reason is that the absorption cross section for the continuum of the B state is appreciably higher than for the continuum of the A state. By heating the nozzle to 533 K the signals which are due to hot band absorption increased at the same rate as the corresponding populations of the higher vibrational levels of the ground state.

In the following the first results of our dimer dissociation studies are summarized.

The composition of the Br_2/Ar molecular beam depends on various parameters such as nozzle geometry, Br_2/Ar gas mixture, · · ·

. . . stagnation pressure and nozzle temperature. It can thus be varied within a wide range. For the investigation of the dimer dissociation we used a 0.1 mm diameter nozzle at room temperature, a temperature of the bromine reservoir of -22°C which corresponds to a vapour pressure of approximately 15 Torr, and a total stagnation pressure of 260 Torr. Under these conditions the ratio of the dimers $[(Br_2)_2]$ in the molecular beam is approximately 11% of the Br_2 concentration. The dimer studies discussed here were performed with the pulsed dye laser at a wavelength of 4844 Å. In this case we investigated the time-of-flight spectra for both Br_2 and Br_3 fragments. In contrast to the monomer dissociation experiments both spectra show a broad peak indicating that the excess energy is distributed among kinetic, vibrational and rotational energy of the fragmentation products. The flight time of the fastest products agrees well with the calculated velocity assuming that all excess energy is transformed into translational energy. The fact that the two spectra do not overlap with respect to the flight time indicates that Br_2 is not just produced by fragmentation in the ionizer from Br_3 but that Br_2 and Br_3 originate from different sources. We conclude that two different dissociation channels occur for the dimer, namely

$$(Br_2)_2 \xrightarrow{h\nu} Br_3 + Br \quad \text{and} \quad (Br_2)_2 \xrightarrow{h\nu} Br_2 + Br + Br^*$$
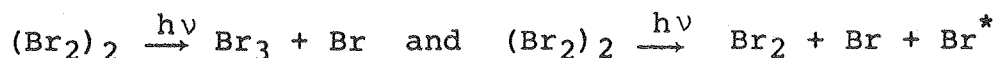
No dependence of the Br_2 and Br_3 time-of-flight spectra on the laser polarization was found. This indicates that the dimer . . .

. . . cannot be a linear molecule. Our results support recent dipole moment measurements on the basis of which an L-shaped structure had been suggested for the bromine dimer [5].

A more detailed report on the subject is in preparation and will be published elsewhere.

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